Preprint
UCRL-JC-136096

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This article was submitted to
3rd International Conference on Gas Hydrates
Salt Lake City, UT
July 18-22, 1999

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

October 25, 1999

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ABSTRACT

Simultaneous measurements of compressional and shear wave speeds through polycrystalline methane hydrate have been made. Methane hydrate, grown directly in a wave speed measurement chamber, was uniaxially compacted to a final porosity below 2%. At 277 K, the compacted material's compressional wave speed was 3650 ± 50 m/s. The shear wave speed, measured simultaneously, was 1890 ± 30 m/s. From these wave speed measurements, we derive Vp/Vs, Poisson's Ratio, bulk, shear and Young's moduli.

INTRODUCTION

Clathrate hydrates of natural gases are nonstoichiometric crystalline solids in which a hydrogen-bonded water lattice is stabilized by individual "guest" molecules encaged in interstitial cavities. Of particular interest is methane (CH_4) hydrate, a structure I hydrate with a unit cell composed of 46 water molecules with 8 cavities available for guest molecule occupation (ideally $CH_4 \cdot 5.75H_20$). Current estimates of CH_4 hydrate distributions suggest vast reservoirs exist in the shallow geosphere (Kvenvolden 1, Holbrook *et al.* 2), and their high CH_4 content has lead to the promotion of hydrates as a potential energy resource. On a localized scale, drilling operations can destabilize hydrate-rich sediments, causing sediment collapse and well bore failures. Hydrate can also break down naturally on larger scales, triggering massive submarine landslides that can displace nearly 4000 km^3 of material, jeopardizing waste-site integrity, cables and other submarine structures (Kvenvolden 1, Campbell 3, Dillon *et al.* 4, Haq 5, Mienert *et al.* 6). Additionally, the effectiveness of CH_4 as a greenhouse gas suggests hydrate stability influences our global climate (Kvenvolden 1, Haq 5, Thorpe *et al.* 7).

Hydrate studies focused on resource management, hazard mitigation, or climate change all require accurate physical property values, which have proven difficult to measure for CH_4 hydrate. There is no consensus in the few published measurements, and most CH_4 hydrate property estimates are based on the behavior of analog materials. Here we describe laboratory measurements of compressional and shear wave speeds (Vp and Vs) through well-characterized CH_4 hydrate grown directly in a wave speed measurement chamber. From our simultaneous Vp and Vs measurements, and by assuming our samples are homogeneous and isotropic, we derive a suite of physical properties for dense, polycrystalline CH_4 hydrate.

EXPERIMENTAL METHOD

Sample Preparation

CH_4 hydrate samples were produced in a custom-built cylindrical pressure vessel (Fig. 1A) by slowly heating granular H_2O ice in a pressurized CH_4 atmosphere, as described by Stern *et al.* (8). Ice used to seed this reaction was grown from triply distilled water, ground and sieved to obtain a 180-250 μm grain size distribution. The resultant CH_4 hydrate is polycrystalline, with random grain orientation, and approximately 28% porosity.

Following synthesis, samples are uniaxially compacted to reduce the porosity below 2%. We estimated the final hydrate porosity from the sample length measured during compaction and the known mass of ice used to seed the experiment. Hydrate extruded during compaction drives our calculated porosity lower than the actual porosity, but we cannot seal the sample chamber prior to compaction because CH_4 gas must be allowed in for hydrate synthesis to occur. To balance our synthesis and compaction requirements, slots are cut in the sample's Teflon jacket. These slots extend 5 mm past the compaction piston into the sample, allowing gas into the sample chamber during synthesis. Rapid piston displacement during the initial stage of compaction blocks these slots off, minimizing hydrate extrusion during the remaining ~10 mm of compaction.

Wave Speed Measurement

Both pressure vessel pistons house a 1 MHz center-frequency piezo-electric transducer (either P- or S- wave) used for pulse-transmission wave speed measurements (Fig. 1B). The transducer remains at atmospheric pressure and supports none of the compressional loading during compaction. An HP Model 214A pulse generator drives the source transducer in the compaction piston, and an HP Model 465A amplifier boosts the signal detected by the transducer in the fixed piston. The signal is displayed on a Tektronix TDS-340 oscilloscope and recorded by a computer running National Instrument's LabView™ data acquisition and display software. Shear and/or compressional wave speed measurements, taken throughout the compaction process, are given by the ratio of sample length to the waveform's time of flight through the sample.

The sample length is calculated from the known dimensions of the pressure vessel and measured position of the compaction piston relative to the pressure vessel. The LCP continuously monitors piston position changes, and periodic measurements of the absolute piston position are made with a depth micrometer to check the LCP results and verify the sample length. Differences between the LCP and depth micrometer results are less than 0.5% of the compacted sample length.

Four methods are used to measure the signal's travel time through the sample. For compacted samples, cross correlation, Hilbert envelope, phase spectral analysis and zero crossing pick results differ by less than 1.5%, our stated velocity uncertainty. Agreement between these different procedures, which utilize different aspects of the measured waveform to estimate the signal travel time, suggest our travel time estimates are independent of the theory by which they are obtained.

RESULTS

To test the validity of our measurement methods, we performed a control experiment on pure, polycrystalline H_2O ice compacted under vacuum at 260 K and uniaxial load of 40 MPa. The recovered H_2O ice sample was translucent, indicating the sample was nearly fully dense, with a final porosity below 1%. Our method reproduces published wave speed results within the scatter of individual studies (Table 1).

Low noise levels in our ice and our hydrate experiments allow us to unambiguously pick arrival times for the precursor P-wave event generated by the S-wave transducer (Fig. 2). In a test using the precursor event, the calculated compressional wave speed through a compacted hydrate sample was indistinguishable from that observed using the dedicated P-wave transducers on a separate sample. This agreement between results obtained using different compressional wave sources on separate samples demonstrates the repeatability of our hydrate synthesis and compaction procedure and shows the S-wave transducer can be used to provide reliable P- and S-wave speed measurements simultaneously.

To draw meaningful conclusions from wave speed comparisons between our results and those already published, it is important to characterize our samples as completely as possible. When forming hydrate from small ice grains warmed in a pressurized methane atmosphere (Stern *et al.* 8), it is possible that a portion of the seed ice will melt rather than form hydrate. Fortunately, there are several indications of incomplete reaction measurable while the sample is in the synthesis

chamber. Pressure and temperature (PT) effects are described in detail by Stern *et al.* (8, 12). In the absence of observable PT effects, x-ray analysis of recovered samples synthesized according to their recipe show <3% ice (Stern *et al.* 8), some of which may have formed during the x-ray analysis.

No PT effects from incomplete reaction were observed during our reported experiments. Though we performed no x-ray analyses on compacted samples, the wave speed measurement itself provides a direct indicator of unreacted material in the sample chamber. Prior to our reported wave speed measurements, our samples are held at 277 K for a minimum of 24 hours. If present, unreacted H_2O would be liquid, tending to lower our wave speed results relative to that expected for pure hydrate. This unreacted water would transform to ice as the compacted sample cools from 277 K to 250 K following our experiment, causing a wave speed increase. No such increase was observed, meaning if unreacted material was present in our experiments, our wave speed measurements were not sensitive enough to be affected. For these reasons, we believe our wave speed results to be representative of polycrystalline CH_4 hydrate.

There are very few published compressional wave speed measurements for CH_4 hydrate, and no shear wave experiments are available for comparison (Table 2). Briefly, Whalley (13) and Pearson *et al.* (14) derive compressional wave speeds for CH_4 hydrate relative to that of ice (Ih) from differences between several mechanical and thermodynamic parameters for the two materials. Shpakov *et al.*'s (15) estimate is based on elastic moduli derived from lattice dynamics investigations of CH_4 hydrate.

On the experimental side, the Site 570 down-hole log result (Mathews *et al.* 16) comes from *in situ* measurements made on DSDP leg 84 after drilling through a three to four meter thick hydrate layer. A meter-long core section recovered from this interval was a solid hydrate mass, largely free of sediment. Brillouin spectroscopy measurements (Whiffen *et al.* 17, Kiefte *et al.* 18) look at the frequency of laser light scattered from thermally induced elastic waves in a clear sample. Producing a clear CH_4 hydrate sample is difficult. As Kiefte *et al.* (18) explain, though they successfully acquired scattered light spectra for several other structure I and II hydrates, only two weak spectra were obtained for CH_4 hydrate. They suggest their weak spectra may stem from the insufficient penetration of focused laser light into their sample.

DISCUSSION

By assuming our samples are homogeneous and isotropic, we can use our simultaneous Vp and Vs measurements to derive additional physical properties. Physical properties for both our ice and hydrate results are compared with published estimates for CH_4 hydrate in Table 3. To obtain our adiabatic moduli values, we used a density of .92 g/cc for ice (Shaw 11), and .90 g/cc for our CH_4 hydrate, which we assume to have a stoichiometry of $CH_4 \cdot 6H_20$. To obtain our isothermal moduli, we used linear expansion coefficients of $52x10^{-6}$ K^{-1} for ice (Whalley 19) and $88x10^{-6}$ K^{-1} for CH_4 hydrate (Kiefte *et al*. 18). For specific heat at constant pressure, we used 2.09 J/g*K for ice (Giauque *et al.* 20), and 2.07 J/g*K for CH_4 hydrate (Handa 21).

CONCLUSION

Differences between our results, based on actual measurements of CH_4 hydrate, and published estimates underscore the importance of making physical property measurements directly on well characterized CH_4 hydrate. Accurate physical property values are essential for planning viable strategies to manage CH_4 hydrate as a global resource and address the challenges it presents. The synthesis procedure developed by Stern *et al*. (8) provides a promising foundation for extending the current description of CH_4 hydrate, and should be considered in the implementation of future thermal and mechanical property measurements on pure CH_4 hydrate or mixtures of CH_4 hydrate with sediment.

ACKNOWLEDGMENTS

This work was supported under NSF grant OCE-97-10506, DOE grants DE-FG03-86ER13601 and DE-FG07-96ER14723, GRI grant 5094-210-3235-1, USGS grant 1434-HG-97-GR-03, NEDO, and an ODP Grad. Res. Fellowship. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

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KEY WORDS

methane, hydrate, wave speed, compressional, shear, bulk, Young's, modulus

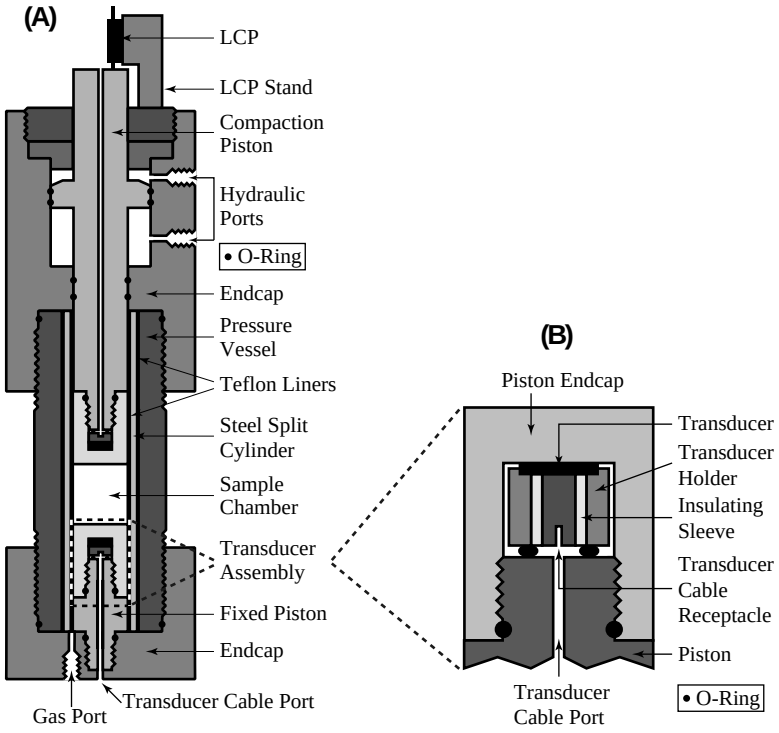

Figure 1. (A) Pressure vessel schematic. Polycrystalline methane hydrate is synthesized directly in the sample chamber, then uniaxially compacted *in situ*. Wave speed measurements are completed without handling the methane hydrate or otherwise removing it from the hydrate stability field. The sample length is monitored using a linear conductive plastic (LCP). (B) Transducer assembly schematic. Using a 1 MHz center frequency S- or P-wave transducer, shear and/or compressional wave speed measurements can be made throughout the compaction process.

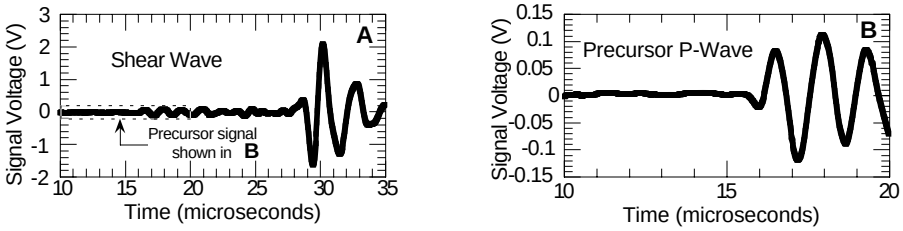

Figure 2. Measured waveforms produced by an S-wave transducer. (**A**) The shear wave signal, arriving near 30 μs, is preceded by a precursor P-wave arriving just after 15 μs (**B**). Low system noise allows use of both waveforms to obtain simultaneous shear and compressional wave speeds.

Table 1. Comparison of compressional (Vp) and shear (Vs) wave speed measurements of polycrystalline H_2O ice (Ih). The wave speeds reported in "This Study" were measured at 260 K after releasing the uniaxial load. The excellent agreement of these values with the known properties of H_2O ice (Ih) demonstrates the reliability of our experimental apparatus and procedure.

Author	Measurement	Vp (m/s)	Vs (m/s)
THIS STUDY	Pulse-Transmission	3900 ± 40	1970 ± 20
Gagnon (9)	Brillouin Spectroscopy	3914	1995
Smith *et al.* (10)	Pulse-Echo	3940	1990
Shaw (11)	Pulse-Transmission	3890	1900

Table 2. Comparison of Vp and Vs wave speed measurements through CH_4 hydrate. Sample compaction reported in "This Study" was conducted at 277 K, with 10 MPa CH_4 pore pressure and a uniaxial load approaching 100 MPa. The final sample porosity was less than 2%. By assuming our samples are homogeneous and isotropic, we can use our simultaneous measurements of Vp and Vs to derive additional elastic parameters (See Table 3).

Author	Measurement	Vp (m/s)	Vs (m/s)
THIS STUDY	Pulse-Transmission	3650 ± 50	1890 ± 30
Pearson *et al*. (14)	Theory	3730 [a]	—
Whalley (13)	Theory	3660 [b]	—
Mathews *et al.* (16)	DSDP Site 570 Log	3600	—
Whiffen *et al*. (17); Kiefte *et al*. (18)	Brillouin Spectroscopy	3400	—
Shpakov *et al*. (15)	Theory	2500	—

[a] Vp should be considered a lower bound for this reference. The reported velocity climbs from 3730 m/s to 3780 m/s as the cage occupancy drops from 100 to 80%. We believe our occupancy rate to be above 90%.

[b] Obtained from Whalley's (13) conclusion that Vp for CH_4 hydrate is 0.939 that of ice, taken from Table 1 to be 3900 m/s.

Table 3. Comparison of elastic property values of polycrystalline H_2O ice, polycrystalline CH_4 hydrate, and published estimates for CH_4 hydrate. None of the prior elastic property estimates for CH_4 hydrate were measured on structure I hydrate (see footnotes).

Property	H_2O Ice THIS WORK	CH_4 Hydrate THIS WORK	Prior Estimates for CH_4 Hydrate
Vp/Vs	1.98 ± 0.02	1.93 ± 0.01	1.95 [a]
Poisson's Ratio	0.33 ± 0.01	0.317 ± 0.006	0.33 [b]
Shear Modulus (GPa)	3.6 ± 0.1	3.2 ± 0.1	2.4 [a]
Adiabatic Bulk Modulus (GPa)	9.2 ± 0.2	7.7 ± 0.2	5.6 [a]
Isothermal Bulk Modulus (GPa)	9.0 ± 0.3	7.1 ± 0.3	—
Adiabatic Young's Modulus (GPa)	9.5 ± 0.2	8.5 ± 0.2	—
Isothermal Young's Modulus (GPa)	9.1 ± 0.3	7.8 ± 0.3	8.4 [b]

[a] These values, from Pandit and King (22), were measured on structure II propane hydrate but are cited elsewhere as estimates of structure I hydrate.

[b] These estimates by Davidson (23) are based on the theoretical work of Whalley (13).